



## ID-TIMS zircons dating, Rb-Sr and Sm-Nd isotope geochemistry of the Paleogene volcanic rocks in the Prekolnitsa graben, SW Bulgaria

### ID-TIMS датиране по циркони, Rb-Sr и Sm-Nd изотопна геохимия на палеогенските вулкански скали от Преколнишкия грабен, ЮЗ България

*Valentin Grozdev<sup>1</sup>, Irena Peytcheva<sup>1,2</sup>, Albrecht von Quadt<sup>2</sup>, Stoyan Georgiev<sup>1</sup>, Rossitsa Vassileva<sup>1</sup>*  
*Валентин Гроздев<sup>1</sup>, Ирена Пейчева<sup>1,2</sup>, Албрехт фон Квадт<sup>2</sup>, Стоян Георгиев<sup>1</sup>, Росица Василева<sup>1</sup>*

<sup>1</sup> Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 24, 1113 Sofia, Bulgaria;  
E-mail: val.grozdev@abv.bg

<sup>2</sup> Institute of Geochemistry and Petrology, ETH, 8092 Zurich, Switzerland

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#### Introduction

The Paleogene volcanic rocks in the Prekolnitsa graben are very well studied in the near past providing information about the field relationships, structural features, petrography and chemistry of the main rock-forming minerals, major element composition and their ages (Ivanov et al., 1971; Arnaudova, 1973; Harkovska, 1974a, b, 1975, 1984, etc.). In a previous study (Grozdev et al., 2010) we presented numerous U-Pb LA-ICP-MS geochronological data on zircons from the volcanic succession that confirm the Paleogene age and largely define the time span of volcanic activity, yet not resolving the temporal relationships of the rocks in the researched area. Present study complements them with precise ID-TIMS U-Pb zircon data and whole rock isotope-geochemistry (Rb-Sr and Sm-Nd) for better understanding the geological history in the basin.

#### Analytical methods

The trace elements were analyzed using LA-ICP-MS at ETH–Zurich and GI–BAS. The whole-rock <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd isotope analyses followed the standard chemical (cation exchange) procedure and are performed on high-resolution TritonPlus mass spectrometer at ETH–Zurich. The ID-TIMS geochronological data are obtained using chemical abrasion and the double-double ET2535 tracer using low-blank laboratories and the TritonPlus mass spectrometer at ETH–Zurich.

#### Geological setting

The area of the studied volcanic rocks extends in western and southern direction from Kyustendil, SW

Bulgaria, being a part of the Ruen zone (Harkovska, 1984). The lithostratigraphic subdivision of the sediments and volcanic rocks in the Prekolnitsa graben is adopted from Harkovska (1974a).

The geological setting of the Prekolnitsa graben includes several stages of volcanic activity. The first stage is marked by volcanic clasts in the basal breccia-conglomerate (Tsarven Dol Formation, the clasts are described also by earlier studies and own observations), followed with lithological transition by the Dolno Selo Formation, composed of sandstones predominantly, which intercalate with small (2–5 cm) polymictic conglomerates and siltstones. The second phase of volcanic activity is observed in the middle and higher parts of the geological profile, presented by pyroclastic materials, interfingering and intercalated with the sandstones. This volcano-sedimentary level (Gyueshevo Formation) is intersected by subvolcanic bodies and flows of fine-porphyrific rhyodacites (Gyueshevo volcanics). The third stage of volcanic activity is presented as an intrusion of a large NW-elongated body of coarse sanidine-phyric trachyrhyodacites (Kopriva volcanics). The final magmatic stage in the graben is connected with felsic rhyolite dykes crosscutting the Kopriva body.

In the Prekolnitsa graben can be distinguished (Grozdev, unpublished data) one more volcanic variety, which crop out in the frame of the Kopriva volcanics as well as a separate volcanic body with the same NW orientation from Pishtilska Mahala toward Bobeshino village. In the past studies, these volcanic rocks were related to the Kopriva volcanics and also described later as part of the Bobeshino magmatic complex (Milovanov et al., 2007). They have very similar geochemical features compared to the Kopriva trachyrhyodacites, but show distinct U-Pb isotopic

Table 1. ID-TIMS ages and isotope data of the studied volcanics

Unit	Rock type	ID-TIMS U-Pb zircon age	$^{87}\text{Sr}/^{86}\text{Sr}_i$	$^{143}\text{Nd}/^{144}\text{Nd}_i/\epsilon_{\text{Nd}}$
Kopriva volcanics	trachyrhyodacites	31.783 ± 0.049 Ma	0.709019–0.709423	–6.48
Gyueshevo volcanics	rhyodacites	32.623 ± 0.047 Ma	0.711199–0.711514	–7.66
Pishtilski volcanics	trachyrhyodacites	32.691 ± 0.042 Ma	0.708838–0.709624	–5.79
Volcanic clasts	(phenorhyolites)	34.63 ± 0.05 Ma	0.707179	–2.23

age. This volcanic stage in the graben will be described here as Pishtilski volcanics (named after the nearby Pishtilska Mahala).

## Geochronology and Isotope Geochemistry

New ID-TIMS geochronological and isotope-geochemical data concern the volcanic clasts, the Gyueshevo, Kopriva and Pishtilski volcanics. The ID-TIMS zircon ages, Rb-Sr and Sm-Nd isotopes are summarised in Table 1.

As shown in Table 1 the  $2\sigma$  error uncertainties of the ID-TIMS Concordia ages are 0.1–0.2% and allow distinguishing geological events within ± 42 000–50 000 years. The ( $^{87}\text{Sr}/^{86}\text{Sr}_i$ ) and ( $^{143}\text{Nd}/^{144}\text{Nd}_i$ ) initial isotope ratios are corrected for 30 Ma, and the latter is presented as  $\epsilon_{\text{Nd}}$ .

## Discussion

A new scenario about the volcanic sequence can be drawn out after ID-TIMS isotopic ages for the rocks from Prekolnitsa graben. The first volcanic activity was no far away from the basin, and lately its volcanic materials were deposited as clasts in the lower formation in the graben. The second volcanic impulse is the intrusion of the Pishtilski volcanics with almost simultaneous emplacement of the Gyueshevo volcanics. The Kopriva volcanics crosscut most of the sedimentary succession and overflow the previously intruded Pishtilski volcanics in the graben. The geological history is probably more complicated than we can assume from our data, but this research is one step further in understanding it.

The  $^{87}\text{Sr}/^{86}\text{Sr}_i$  isotope ratio of the studied rock shows that the volcanic clasts ( $^{87}\text{Sr}/^{86}\text{Sr}_i$  0.707) have Lower continental crust signature or suggest mantle-crust interaction; the Kopriva and Pishtilski volcanics have mantle/crust affinity ( $^{87}\text{Sr}/^{86}\text{Sr}_i$  0.709) further modified by the crust; and the Gyueshevo volcanics isotope characteristics ( $^{87}\text{Sr}/^{86}\text{Sr}_i$  0.711) are more typical of the Upper continental crust. The  $\epsilon_{\text{Nd}}$  parameter points out that the volcanic clasts are from considerably different source ( $\epsilon_{\text{Nd}}$  –2.23) compared to the volcanic rocks from the graben. The Kopriva and Pishtilski volcanics have similar  $\epsilon_{\text{Nd}}$  values, while the Gyueshevo volcanics reveal slightly deeper negative values. The resemblance of Sr and Nd isotope characteristics of

the Kopriva and Pishtilski volcanics suggest that they are formed by melting of analogues substrate in the continental crust. The Gyueshevo volcanics have very similar isotope composition to the Ossogovo granite ( $^{87}\text{Sr}/^{86}\text{Sr}_i$  0.711125 and  $\epsilon_{\text{Nd}}$  –7.64; Grozdev, unpublished data) and infer similar magma source (the same magma chamber/geochemical reservoir) with more continental input.

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